Toward a Comprehensive Model of Snow Crystal Growth Dynamics:

1. Overarching Features and Physical Origins

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Abstract. We describe a comprehensive model for the formation and morphological development of atmospheric ice crystals growing from water vapor, also known as snow crystals. Our model derives in part from empirical measurements of the intrinsic ice growth rates as a function of temperature and supersaturation, along with additional observations and analyses of diffusion-driven growth instabilities. We find that temperature-dependent conformational changes associated with surface melting strongly affect layer nucleation dynamics, which in turn determines many snow-crystal characteristics. A key feature in our model is the substantial role played by structure-dependent attachment kinetics, producing a growth instability that is largely responsible for the formation of thin plates and hollow columnar forms. Putting these elements together, we are able to explain the overall growth behavior of atmospheric ice crystals over a broad range of conditions. Although our model is complex and still incomplete, we believe it provides a useful framework for directing further investigations into the physics underlying snow crystal growth. Additional targeted experimental investigations should better characterize the model, or suggest modifications, and we plan to pursue these investigations in future publications in this series. Our model also suggests new avenues for the continued exploration of ice surface structure and dynamics using molecular dynamics simulations.

1 Introduction

Laboratory observations of snow crystals dating back to the 1930s have revealed a complex dependence of growth morphologies on temperature and supersaturation [1, 2]. Under common atmospheric conditions, for example, ice crystals typically grow into thin plate-like forms near -2 C, slender columns and needles near -5 C, thin-walled hollow columns near -7 C, very thin plates again near -15 C, and columns again below -30 C. In addition, morphological complexity generally increases with increasing supersaturation at all temperatures. These observations are often summarized in the well-known Nakaya morphology diagram, and one example is shown in Figure 1 [1]. Extensions to lower temperatures, as well as more detailed morphological studies, can be found in the literature [3, 4, 5].

Although the overall features and morphological transitions seen in the Nakaya diagram have been well established empirically, a basic physical explanation of why snow crystals exhibit this growth behavior has been surprisingly elusive. In particular, the fact that snow crystals alternate between plate-like and columnar forms as a function of temperature has been an outstanding problem for nearly 75 years. The purpose of this paper is to present a new model for ice growth from water

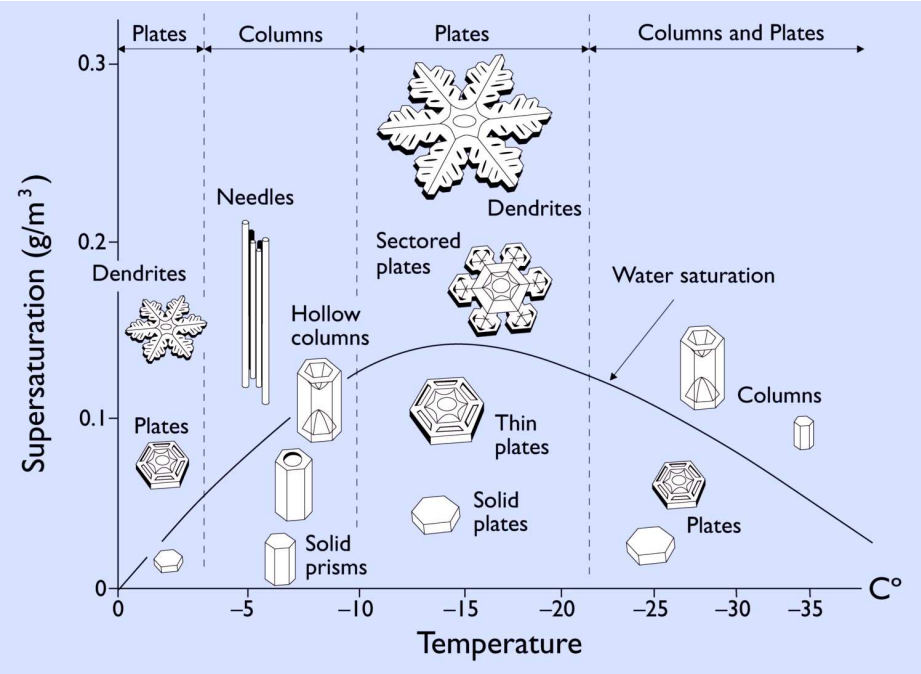

Figure 1: The Nakaya snow crystal morphology diagram, showing different types of snow crystals that grow in air at atmospheric pressure, as a function of temperature and water vapour supersaturation relative to ice. The water saturation line gives the supersaturation of supercooled water, as might be found within a dense cloud. Note that the morphology switches from plates ($T \approx -2$ C) to columns ($T \approx -5$ C) to plates ($T \approx -15$ C) to predominantly columns ($T < -30$ C) as temperature is decreased. Temperature mainly determines whether snow crystals will grow into plates or columns, while higher supersaturations generally produce more complex structures.

vapor that includes physical mechanisms that can explain the observed morphological behavior. Although our model is not simple, and details are still missing, we believe it provides a reasonable overarching picture of the various physical processes that define the growth dynamics of atmospheric snow crystals.

Progress toward explaining how complex structures arise spontaneously during solidification has generally been hard won. The problem is exacerbated by the fact that numerous physical processes are often involved over many length scales, and these work in concert to produce the observed structures. Identifying and characterizing the most important of these processes, quantifying them with suitable numerical algorithms, and merging the pieces into a comprehensive model of structure formation has been an ongoing process for many decades.

It has been known since the mid-1960s, for example, that dendritic structures arise from the Mullins-Sekerka instability during diffusion-limited growth [6]. Producing a quantitative model of this process required substantial theoretical effort, however, culminating in the development of solvability theory during the 1980s [7, 8]. With this we learned that the overall branching scale is set by seemingly minor anisotropies in the surface dynamics. The surface energy anisotropy plays

the key role in the case of solidification from the liquid phase, while for solidification from gaseous precursors the anisotropy in the surface attachment kinetics is typically the more dominant factor [1, 9].

Numerical models of diffusion-limited growth were developed about the same time as solvability theory, including front-tracking and phase-field techniques [10, 11]. These methods have enjoyed considerable success in reproducing dendritic structures arising during solidification from the melt, such as in metallurgical systems or ice growth from liquid water. These systems work well computationally in part because the material anisotropies are typically quite small, with surface energy differences of perhaps a few percent between faceted and non-faceted surfaces. For such systems the growth structures are generally smooth and free of sharp corners or edges, and numerical models tend to be robust and stable.

In growth from the vapor phase, anisotropies in the surface attachment kinetics are often very large, resulting in dendritic structures that are not smooth with continuous derivatives, but are instead strongly faceted with sharp edges. In this case numerical instabilities can be problematic, so considerably more care is required to produce stable growth models [12]. As a result, the usual numerical techniques used for studying diffusion-limited growth have not yet been able to produce satisfactory snow crystal structures from reasonable physical inputs.

In 2008-9, Gravner and Griffeath developed cellular automata (CA) techniques that avoided the numerical instabilities that affected other methods [13, 14]. These CA models have generated full three-dimensional dendritic structures that reproduced many characteristics of natural snow crystals, including growth forms that are both branched and faceted, with sharp edges. Cellular automata models incorporating more physically derived rules have since been demonstrated [15], and with suitable inputs it now appears possible, at least in principle, to realize a numerical model that can accurately reproduce snow crystal growth rates and morphologies at all temperatures and supersaturations.

Analysis of diffusion-limited growth using these theoretical and computational tools has yielded numerous insights into the dynamics of structure formation. For example, solvability theory nicely explains why the tip velocity of a growing dendritic structure depends linearly on supersaturation for solidification from vapor, while a quadratic dependence on undercooling is typical for growth from the liquid phase [1, 9]. In addition, scaling relationships in diffusion-limited growth models provide an explanation for the increase in structural complexity that accompanies decreasing vapor diffusion rates [15, 16].

For snow crystal growth, these theoretical considerations generally explain why morphological complexity increases with supersaturation, crystal size, and background gas pressure. Thus the observed variation along the supersaturation axis on the morphology diagram in Figure 1 is fairly well understood, at least at a qualitative level. Producing accurate model crystals using sensible input physics over a range of conditions has not yet been accomplished, and some unusual dendritic snow crystal structures may be quite challenging to reproduce [17]. Nevertheless, diffusion-limited growth – the underlying physical mechanism responsible for the formation of much snow crystal structure – is reasonably well understood, and satisfactory computational algorithms describing this process are available.

The ability to make high-fidelity numerical models of dendritic growth is only the first step, however, since models require inputs. For the snow crystal case, one of the most important physical inputs comes from the many-body interactions that determine how water molecules are incorporated into the crystalline lattice, referred to as the *surface attachment kinetics*. For a rough surface, this incorporation is essentially instantaneous for all molecules that strike the surface. But the attachment

to faceted surfaces is much slower, and in snow crystal formation the attachment kinetics are often as important as diffusion in governing the morphological development. Therefore, understanding the growth of faceted ice surfaces is essential for any snow crystal model.

Some relevant physical processes that occur during ice crystal growth from vapor include the adsorption and evaporation of surface admolecules, their diffusion along the surface, the nucleation of new molecular layers, and the Gibbs-Thomson effect. Near the melting point one must also consider the high vapor pressure of ice, along with temperature-dependent surface structural effects associated with surface melting [18]. Characterizing the many-body physics of these various effects remains a significant challenge.

The surface attachment kinetics for ice are sufficiently complex that crystal growth rates cannot yet be determined from *ab initio* molecular dynamics modeling, and it appears that this direct approach will be unfeasible for the foreseeable future. Nevertheless, one need not track every molecule to create a reasonable physical picture of the crystallization process, or to realize a useful parameterization of crystal growth rates. Another route is to combine basic theoretical considerations with empirical data to create a more simplified crystal growth model, hopefully one that explains the morphology observations with as much quantitative accuracy as possible.

Statistical models of crystal growth dynamics have been developed over many decades also, and some notable early advances in this area include the formulation of classical nucleation theory, as well as the role of screw dislocations in crystal growth (for example, see [19]). The former is especially important in snow crystal growth, while the effects of dislocations are often negligible [26]. Crystal growth theory has generally enjoyed much success describing many faceted materials, especially cases where the surface structure is very stable and the admolecule dynamics are especially simple.

Unfortunately, the ice surface has a high equilibrium vapor pressure, which means that the surface is in a highly dynamical state. Under typical conditions, for example, ice molecules evaporate from and redeposit onto the surface at rates of order one monolayer per microsecond, while crystal growth rates can easily be 4-6 orders of magnitude slower. Add the conformational changes associated with surface melting, and it is easy to see why understanding the molecular physics of ice crystal growth presents some unique theoretical challenges.

Because the ice surface dynamics are only poorly understood, snow crystal growth models to date have been quite speculative in nature. Some early models in the 1960s focused on surface diffusion rates and step growth velocities, and how these depended on temperature for the principal facet surfaces (for a review, see [20]). This approach now appears to be incorrect, as subsequent experiments have shown that the nucleation of new molecular layers on the principal facet surfaces is the rate-limiting step in their growth. Recent evidence for this will be discussed below.

One of the best previous attempts to create a comprehensive and physically motivated model of snow crystal growth was that presented by Kuroda and collaborators in the 1980s [21, 22, 23]. This model describes a qualitative picture of the influence of surface melting on crystal growth rates, and how temperature-dependent surface melting could explain the observed spectrum of growth morphologies. Subsequent experimental data have not supported this model, but the underlying assumption that surface melting plays an important role appears to be sound.

More recent experimental and modeling efforts have convincingly demonstrated that layer nucleation plays an important role in the formation of faceted ice surfaces (see [24, 26] and references therein), as had been assumed in the Kuroda model and in some earlier models. Moreover, it has certainly been demonstrated that bulk diffusion through the surrounding gas is a key factor influencing growth rates [25]. To date, however, no model has convincingly explained, even in a qualitative fashion, the temperature dependence seen in the Nakaya morphology diagram.

Our approach to this problem has been to use quantitative growth measurements to guide our model building efforts, and to use numerical CA modeling to compare data with calculated growth rates and morphologies over a range of conditions. We first observed growth rates at reduced background pressures to nearly eliminate bulk diffusion effects, thus giving measurements of the intrinsic growth rates of the ice facet surfaces. With these data in hand, we then examined growth rates and morphologies at normal atmospheric pressures, thereby allowing a quantitative analysis of diffusion-driven growth instabilities. Our result is a comprehensive model that agrees with the most reliable growth data and explains the general features in the snow crystal morphology diagram.

Although our model is not without speculative elements, we feel it is a significant improvement over previous attempts. The model provides a useful overarching picture of the underlying physics, as well as a reasonable framework for continued discussion of this problem. For example, we have found that a key quantity in our model is the step energy β associated with the edge of a molecular terrace on the facet surfaces. As β is a molecular-scale, equilibrium property of the crystal surface, its calculation should be much easier than full dynamical calculations of crystal growth rates. Thus it may be possible to use current *ab initio* modeling techniques to examine some aspects of snow crystal growth down to the molecular scale.

We have also found that our model is very useful for suggesting targeted experimental investigations that can both test the model predictions and better determine the model parameters. In such a capacity, we believe it likely that continued investigation of this model will be fruitful, and may yield new insights into ice growth dynamics in different circumstances. We are currently working on several such experiments, and the results from these will be presented in future publications in this series.

2 Intrinsic Growth of the Principal Facets

An important step toward understanding snow crystal growth dynamics is to quantify the growth rates of the principal facet surfaces as a function of temperature and supersaturation. Following the notation in [1], we parameterize the surface growth velocities using $v = \alpha v_{kin} \sigma_{surf}$, where v is the perpendicular growth velocity, $v_{kin}(T)$ is a temperature-dependent "kinetic" velocity derived from statistical mechanics, and σ_{surf} is the water vapor supersaturation relative to ice at the growing surface. The attachment coefficient α, which depends on T, σ_{surf}, and other factors, encapsulates the attachment kinetics governing crystal growth at the crystal/vapor interface. From the definition of v_{kin}, we must have $\alpha \leq 1$.

For the simplest case – the growth of an infinite, clean, dislocation-free faceted ice surface in near equilibrium with pure water vapor at a fixed temperature – the attachment coefficient is well defined and we must have a unique $\alpha(\sigma_{surf}, T)$ for each facet surface. We refer to the $\alpha(\sigma_{surf}, T)$ for the two principal facets in this ideal case as the "intrinsic" attachment coefficients.

We determined $\alpha(\sigma_{surf}, T)$ through a lengthy series of measurements of crystals growing on a substrate at low background pressure. Experimental details, the resulting data and analysis, and references to prior work measuring $\alpha(\sigma_{surf}, T)$, can be found in [26]. Over the temperature range -2 C $> T > -40$ C, our growth data are well described by a dislocation-free layer-nucleation crystal growth model, which we parameterize using $\alpha(\sigma_{surf}, T) = A \exp(-\sigma_0/\sigma_{surf})$. The measured parameters $A(T)$ and $\sigma_0(T)$ for the basal and prism facets are shown in Figure 2.

The data in Figure 2 are the most recent, most extensive, and we believe the most accurate measurements to date of the intrinsic $\alpha(\sigma_{surf}, T)$ for the principal facets of ice. Several sources

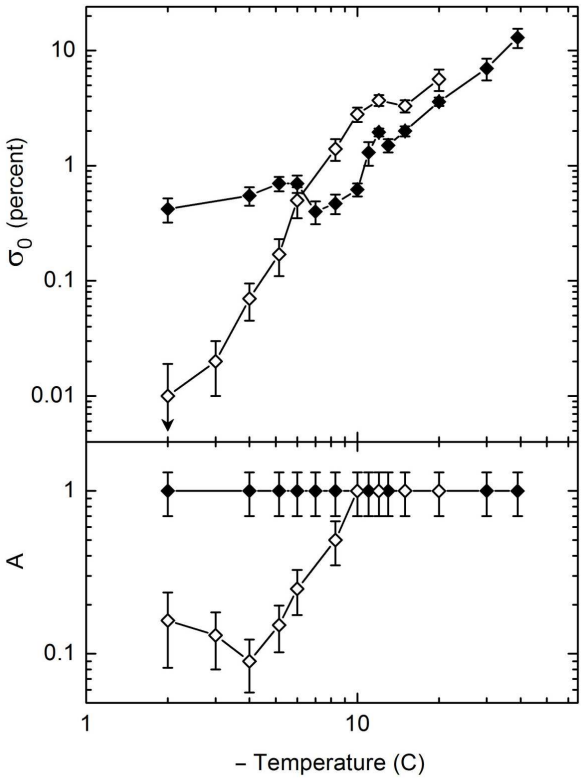

Figure 2: Measurements of the intrinsic growth rates of the principal ice crystal facets. The growth velocity normal to the surface is described by $v = \alpha v_{kin} \sigma_{surf}$, where σ_{surf} is the supersaturation at the surface and the attachment coefficient is parameterized with $\alpha(T, \sigma_{surf}) = A \exp(-\sigma_0/\sigma_{surf})$. The solid points show the measured $A(T)$ and $\sigma_0(T)$ for the basal facets, while the open points show measurements of the prism facets, from [26].

of potential systematic errors were examined with greater care than had been done in previous experiments, including effects from substrate interactions and bulk diffusion, and these errors were largely eliminated. Possible errors from chemical contamination of the ice surface were examined as well [27]. Within the stated error estimates, therefore, we assume that the data in Figure 2 represent empirical fact that must be incorporated within our model of snow crystal growth dynamics.

2.1 Physical Origins - I

Our understanding of the detailed molecular structure and dynamics of the ice surface is not sufficient to provide a full physical explanation of the measurements displayed in Figure 2, and *ab initio* molecular dynamics simulations cannot accurately calculate ice growth rates directly [28, 29, 30]. However, the problem is greatly simplified with the realization that classical nucleation theory dictates that the parameter $\sigma_0(T)$ derives from the step energy $\beta(T)$ associated with the edge

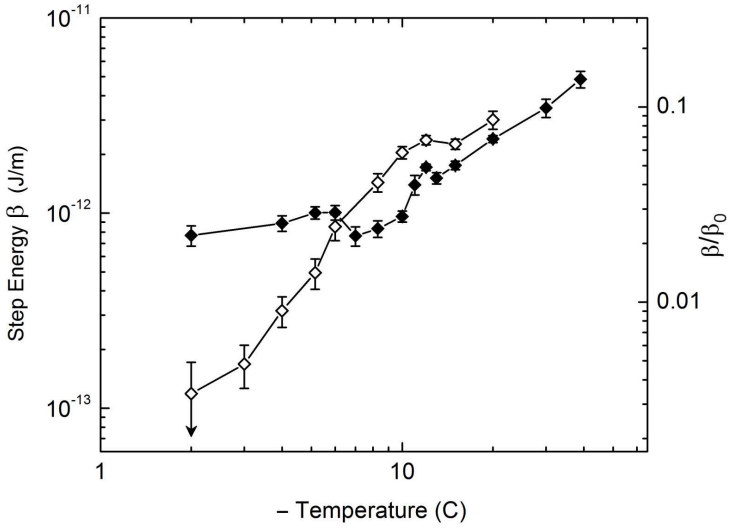

Figure 3: The step energy $\beta(T)$ associated with the edge of a molecular terrace for the two principal facets of ice. This quantity was derived from the measured $\sigma_0(T)$ in Figure 2 using classical nucleation theory [26]. For comparison we also show β relative to $\beta_0 = \gamma a$, where γ is the ice surface energy and a is the molecular step height, as described in the text.

of a molecular terrace on the facet surface [19]. Using this theory, we are able to convert the measurements to give $\beta(T)$ for both facets, as shown in Figure 3 [26].

By taking advantage of nucleation theory, we are thus able to reduce the problem of crystal growth to one of determining of the step energy. This represents a major simplification of the problem, since crystal growth is a complex dynamical process, while the step energy is a basic equilibrium property of the ice surface. Although $\beta(T)$ has not yet been calculated from existing ice surface models, this goal may be reached in the near future. As part of our model, we suggest the following qualitative picture of how temperature-dependent surface melting can explain much of the detail seen in Figure 3.

Beginning at the lowest temperatures in Figure 3, we see that $\beta(T)$ increases monotonically with decreasing temperature for both facets below $T = -15$ C. For extremely low temperatures, we would expect that the ice surface structure would approach that of a simple molecular layer model (essentially a basic Kossel crystal [31]), so the step energy would approach $\beta \approx \beta_0 = \gamma a$, where γ is the ice surface energy and a is the step height. This follows because in a simple layer model the increased surface area associated with a step is aL, where L is the step length, so the increase in effective surface energy is γaL, giving $\beta \approx \gamma a$.

This reasoning suggests that $\beta \to \beta_0$ at very low temperatures, and we consider this to be a prediction of our model. Additional experiment and theory could be used to confirm this hypothesis. As temperature is increased, we would expect that thermal fluctuations would influence the structure of the terrace step, causing a surface reconstruction that effectively smooths out the step, reducing β. Thus we would expect β to decrease monotonically with increasing temperature, with $\beta/\beta_0 < 1$,

and this behavior is seen in Figure 3 for $T < -15$ C.

Because the step energy β is a molecular-scale equilibrium property of the ice surface, similar in this regard to the surface energy γ, it appears promising that β may be calculable using molecular dynamics simulations. The low-temperature region is probably the most amenable to such investigations, since for $T < -15$ C it appears that the surface structure is relatively simple and not complicated by substantial surface melting. If the measured approximate power-law behavior in $\beta(T)$ could be reproduced for the low-temperature region, this would give one confidence that our characterization of the step energy is a reasonable one, as well as providing physical insights into the underlying molecular origins of $\beta(T)$.

Continuing up in temperature in Figure 3, we see unusual features in both β_{basal} and β_{prism} at $T \approx -12$ C. A sharp peak in $\beta_{basal}(T)$ is seen at this temperature, as is a broader peak (little more than a shoulder) in $\beta_{prism}(T)$. Both peaks are robust features in our data, and we suggest that both are associated with the onset of significant surface melting in the ice surface. By "onset" in this context, we mean the temperature at which surface melting first begins to significantly affect the crystal growth dynamics. This interpretation is consistent with some other measurements of surface melting in ice [32], although in general our theoretical understanding of surface melting in ice and other materials is rather poor [18].

Exactly why the onset of surface melting produces peaks in $\beta(T)$ near -12 C is not known. We can only speculate that the observed behavior may result from complex many-body dynamics at this temperature, when the top molecular layers are just beginning to become disordered. If this is true, then explaining these -12 C features in detail may be quite challenging. Their effect on snow crystal growth dynamics, however, appears to be fairly small compared to the overall behavior in $\beta(T)$ for the two facets.

Focusing now on the prism facet, we see in Figure 3 that $\beta_{prism}(T)$ declines precipitously with increasing temperatures above $T \approx -10$ C. At these temperatures, surface melting produces a substantial quasi-liquid layer (QLL) in ice, so the ice/vapor interface becomes replaced by an ice/QLL/vapor interface. The data then suggest that surface reconstruction further smooths the step edge on the prism facet, thereby reducing β_{prism} with increasing temperatures. Here again the situation seems ripe for additional investigation with molecular dynamics simulations. Investigations using *ab initio* calculations have yielded considerable insights into ice surface melting [28, 29, 30], and and it seems promising that examining step energies with these methods may well explain some of the features seen in Figure 3.

For the basal facet, we see that $\beta_{basal}(T)$ initially drops for temperatures above $T \approx -10$ C, but then the trend reverses and $\beta_{basal}(T)$ exhibits a brief upward jump with increasing temperature for $T \approx -6.5$ C, finally leveling off for $T > -4$ C. To explain this behavior, we borrow a key feature from the Kuroda model and suggest that extensive surface melting at higher temperatures yields a sharp ice/QLL interface on the basal facet. We suggest that this interface is accompanied by a β_{basal} that approaches some constant value as the temperature approaches the melting point and the QLL thickness diverges. In this behavior we see an important difference between the basal and prism facets of ice – near the melting point, the nucleation barrier essentially vanishes on the prism facet (its effects become negligible in the crystal growth dynamics) while remaining substantial on the basal facet.

2.1.1 Connection to Ice Growth from Liquid Water

This high-temperature picture is consistent with observations of ice growing from liquid water, where one typically sees faceting on the basal facet but no faceting on the prism facet [33]. This makes sense given our understanding that the QLL thickness diverges near the melting point, so one expects similar nucleation barriers at the ice/water interface and the ice/QLL interface when the QLL thickness is large.

Another prediction from our model, therefore, is that there should be a correspondence between β_{basal} near the melting point as determined from two different measurement strategies – using ice growth from water vapor, and using ice growth from liquid water. To our knowledge, this correspondence has not been investigated to date. Experiments on ice growth from liquid water have not yet determined β_{basal} accurately [33], mainly because of interference from heat diffusion effects. But it appears that an accurate measurement of β_{basal} for the liquid case could be achieved with a targeted experimental investigation. Examining the correspondence between growth from water vapor near 0 C and growth from liquid water at low supercoolings may well yield additional insights into the attachment kinetics in both cases.

2.1.2 Surface Diffusion and $A(T)$

Early attempts to model the temperature dependence in snow crystal growth focused on the 2D diffusion of water admolecules on the ice surface, as mentioned above and discussed at length in [20]. The measurements in Figure 2 tell us, however, that surface diffusion plays a relatively minor role compared to nucleation dynamics. From crystal growth theory in a multinucleation model (see [19]), we find that the growth parameter $\sigma_0(T)$ is determined mainly by the step energy $\beta(T)$, while the prefactor $A(T)$ is determined mainly from the surface diffusion of admolecules and their attachment to the terrace edges. (Note that we have ignored a factor of $\sigma_{surf}^{1/6}$, as this factor is typically inconsequential compared to the nucleation factor $\exp(-\sigma_0/\sigma_{surf})$.) Since $A(T)$ derives from an extrapolation of the growth data to high σ_{surf} [26], and is further subject to the constraint that $\alpha \leq 1$, we see that fast surface diffusion yields the limit $A(T) = 1$, as is observed on the prism facet for $T \leq -10$ C and on the basal facet at all temperatures measured.

From Figure 2 we see that $A_{prism}(T)$ is less than unity only for $T > -10$ C, when surface melting is well developed. We suggest that A_{prism} is reduced in this region because of a growth impedance at the ice/QLL interface, although the microphysics underlying this is not known. Additional investigation of this behavior, and comparison with other crystal systems, would likely be fruitful.

At temperatures near $T = -2$ C, the nucleation barrier on the prism facet is quite low, so the main impediment to the intrinsic growth of the prism facet comes from the fact that $A_{prism} < 1$. Because of this, the growth of the prism facet is slower than a rough surface, which results in faceting. In growth from liquid water we see no faceting of the prism facet, however. This suggests another prediction of our model, that $A_{prism}(T \to 0) \approx 1$, owing to the correspondence between growth from liquid water and growth when the QLL is thick. Extending the data in Figure 2 to higher temperatures, although challenging experimentally, could test this prediction.

2.2 Further Investigations of Intrinsic Growth Rates

Although the data in Figure 2 represent a significant step forward in understanding the intrinsic growth behavior of the principal facets of ice, extending these measurements to both lower and

higher temperatures would be beneficial. The low-temperature regime is probably the easiest to model with molecular dynamics simulations, so better measurements here could facilitate progress in characterizing the ice surface in the absence of surface melting. Reproducing the observed $\sigma_0(T)$ with *ab initio* calculations would be a substantial achievement, even if only in the low-temperature regime, given our current poor understanding of the molecular structure and dynamics of the ice surface.

At the high-temperature end of the spectrum, comparing ice growth from water vapor and from liquid water would also likely be fruitful. Better data are needed for both systems, and the theory describing the correspondence needs to be developed. Comparing the ice/water and ice/QLL interfaces would certainly help develop our knowledge of these interfaces, as well as improving our overall understanding of surface melting in the thick-QLL limit.

Although the physical picture we have painted above is imperfect and somewhat speculative, we believe it provides a useful framework for further investigations. Our intention in defining this model is in part to create a plausible qualitative description of the underlying physics that is consistent with the experimental data. In spite of its shortcomings, we believe that our model of the intrinsic growth behavior does make some useful predictions, described above, as well as suggesting additional targeted investigations, both experimental and theoretical.

3 Structure Dependent Attachment Kinetics

The measured intrinsic growth rates, as parameterized above and displayed in Figure 2, immediately appear to contradict many details in the Nakaya morphology diagram. For example, we see that $\sigma_{0,basal} < \sigma_{0,prism}$ at -15 C, implying that $\alpha_{prism} < \alpha_{basal}$ for all supersaturations at this temperature. This inequality suggests that columnar prisms would be the preferred growth morphology, while it is well established that thin plates form at this temperature.

This discrepancy is explained in our model with the phenomenon of *structure-dependent attachment kinetics* (SDAK) [35, 36, 37], which causes the attachment coefficient $\alpha(\sigma_{surf})$ to depend on the mesoscale morphological structure of the ice surface itself. For example, our SDAK model at -15 C assumes that α_{prism} on a thin plate edge is higher than the corresponding "intrinsic" α_{prism} for a large faceted surface. The increased α_{prism} then reverses the above inequality, yielding $\alpha_{prism} > \alpha_{basal}$ and resulting in the growth of thin plates.

More specifically, in our SDAK model the increase in α_{prism} on the edge of a thin plate arises because $\sigma_{0,prism}$ decreases as the width of the final molecular terrace on the prism surface approaches molecular dimensions. Observations indicate that the radius of curvature of the edge of a thin plate at -15 C is typically $R \approx 0.5$ μm, so the width of the last molecular terrace on the prism surface is roughly $w \approx (aR)^{1/2} \approx 40a$, where $a \approx 0.3$ nm is the size of a water molecule. The fundamental premise of our SDAK model is that surface melting and perhaps other structural effects will become altered on such a narrow terrace, affecting the nucleation dynamics. Since the nucleation of new molecular layers on this thin terrace largely determines the growth rate of the prism edge, it follows that SDAK effects play an important role in governing ice growth morphologies.

Here again, our detailed understanding of the ice surface is not sufficient to define a incontrovertible model of structure dependent attachment kinetics from first principles. However, growth measurements do demonstrate the existence of this phenomenon [37], and these same measurements can characterize the SDAK effects to some degree. We proceed with the understanding that our SDAK model is quite preliminary at present. Additional measurements and theoretical work will be

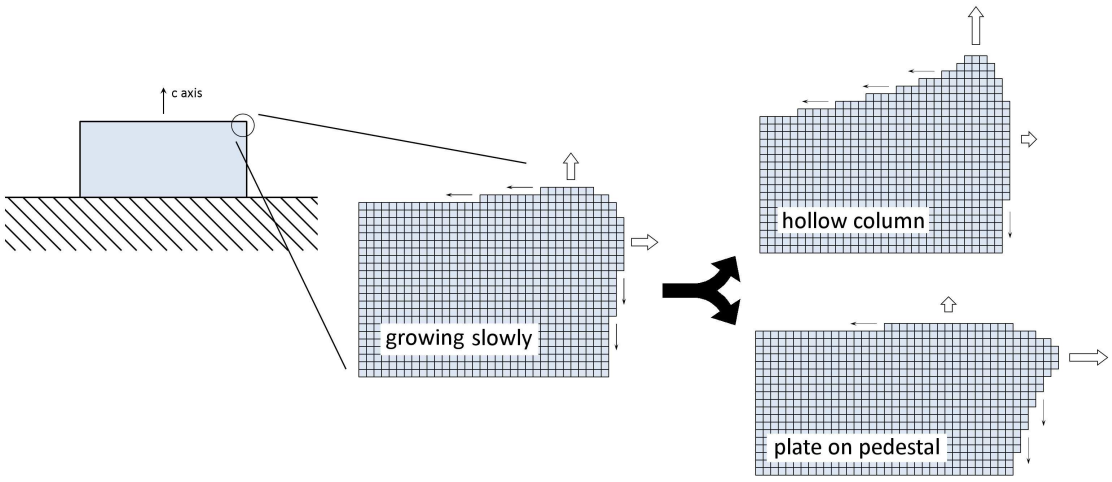

Figure 4: A schematic depiction of the SDAK instability described in the text. The growth of the corner of a faceted ice crystal prism (left) is dominated by the nucleation of terraces on the basal and prism facets (center). If the nucleation rate increases as the width of the top basal terrace decreases (top right), in keeping with the SDAK model, then the accelerated growth narrows the basal surface, accelerating the growth still more. The resulting positive feedback generates the growth of a hollow columnar crystal. If the same SDAK effect is more prevalent on the prism facet (lower right), then the instability leads to the growth of a thin plate from the top edge of the prism.

necessary to understand the importance of SDAK effects on both facets as a function of temperature to a satisfactory level.

3.1 An Edge-Enhancing SDAK Instability

A key feature of our SDAK hypothesis is that it leads to an edge-enhancing growth instability. The essential mechanism is that as a thin edge begins to form, σ_0 decreases and thus further increases the edge growth rate. The enhanced growth causes the edge to sharpen, which again increases the growth rate. This positive feedback yields a growth instability that enhances the formation of sharp edges.

To examine the SDAK instability in more detail, consider the growth of an initially isometric prism on a substrate, depicted in Figure 4. We assume the presence of an inert background gas surrounding the crystal, so the growth is partially diffusion limited. If the crystal is growing slowly (center diagram in the figure), then molecular terraces nucleate slowly near each corner of the crystal, where σ_{surf} is locally highest, and steps propagate away from the corner. The corner itself is rounded from the Gibbs-Thomson effect. For slow growth, this is essentially the standard model of diffusion-limited faceted crystal growth, resulting in slightly concave faceted surfaces.

Consider now the highest molecular terrace on either facet next to the growing corner. As the supersaturation is increased, new terraces nucleate more frequently, so the average width of the top terrace decreases. As the SDAK effect reduces σ_0 on narrower terraces, the nucleation rate increases

and in turn the more rapid growth further decreases the width of the top terrace.

At this point a competition occurs between growth on the basal and prism facets, as shown in the pair of diagrams on the right side of Figure 4. If the SDAK effect preferentially reduces σ_0 on the basal facet (top right diagram), then the basal growth is especially enhanced. Because the growth is also diffusion-limited, the fast growth on the basal facet depletes the water vapor supply from the nearby prism facet. This decreases the nucleation rate on the prism facet, which causes the average width of the top terrace to increase, which in turn increases $\sigma_{0,prism}$. The combined effect is that $\sigma_{0,prism}$ increases to essentially its intrinsic value while $\sigma_{0,basal}$ grows ever smaller as the basal edge grows sharper. The final result is a hollow column morphology with thin basal edges. Alternatively, the same instability could favor the prism facets, as seen in the lower right diagram in Figure 4. In this case a thin plate-like crystal would form on the isometric prism, producing a "plate-on-pedestal" morphology [37].

Note that the SDAK instability nicely explains the abrupt transitions between plate-like and columnar growth seen in the morphology diagram. Relatively small changes in the surface attachment kinetics with temperature can be amplified via the SDAK instability to yield very substantial changes in the final crystal morphologies.

Note also that the SDAK instability is essentially an extension of the well-known Mullins-Sekerka instability in diffusion-limited growth [6]. The latter is well known for producing dendritic branching during solidification, but alone it does not explain the formation of thin plate-like or hollow columnar crystals. Thin-edge morphologies require strong anisotropies in the attachment kinetics – namely $\alpha_{prism} \gg \alpha_{basal}$ for thin plates or $\alpha_{prism} \ll \alpha_{basal}$ for hollow columns. The SDAK instability provides a natural mechanism to generate these strong anisotropies.

3.2 Physical Origins - II

The SDAK effect is difficult to fully evaluate using growth measurements alone, in part because of the SDAK instability. For example, the strong SDAK effect on the prism surfaces at -15 C promotes the growth of thin plates at this temperature, which in turn means that the basal facets are quite large. If an SDAK effect were present on the basal facets at -15 C, we could not see it because it is essentially overshadowed by the stronger SDAK effect on the prism surfaces. The bifurcation into plate-like or columnar growth shown in Figure 4 means that only the dominant SDAK effect can be characterized by growth measurements at a given temperature.

We propose that the strong SDAK effect on the prism facet at -15 C is related to the precipitous drop in $\sigma_{0,prism}$ for temperatures above -10 C. When a prism facet becomes very narrow at -15 C, we suggest that the molecular binding in the top terrace is effectively reduced relative to the binding on a larger facet surface. This reduced binding causes an increase in surface melting, which in turn causes a decrease in $\sigma_{0,prism}$, as one normally sees at higher temperatures. Thus the function $\sigma_{0,prism}(T)$ is essentially shifted in temperature when the prism terrace becomes narrow. Although the details of this behavior are uncertain, we suggest that $\sigma_{0,prism}(T)$ on the top terrace of a thin edge looks something like the dotted line shown in the lower panel in Figure 5.

With this picture, we see that the SDAK effect will be less prevalent on a prism facet below -20 C, because a larger effective shift in temperature would be needed to substantially reduce $\sigma_{0,prism}$, and such large shifts are not provided by the SDAK mechanism. Thus in Figure 5 we see that $\sigma_{0,prism,SDAK} \approx \sigma_{0,prism}$ at -20 C. Put another way, the SDAK effect on the prism facet is most prevalent when the temperature is close to the drop-off in $\sigma_{0,prism}$ associated with surface melting. At temperatures below -20 C, reducing the width of the prism facet is not sufficient to induce surface

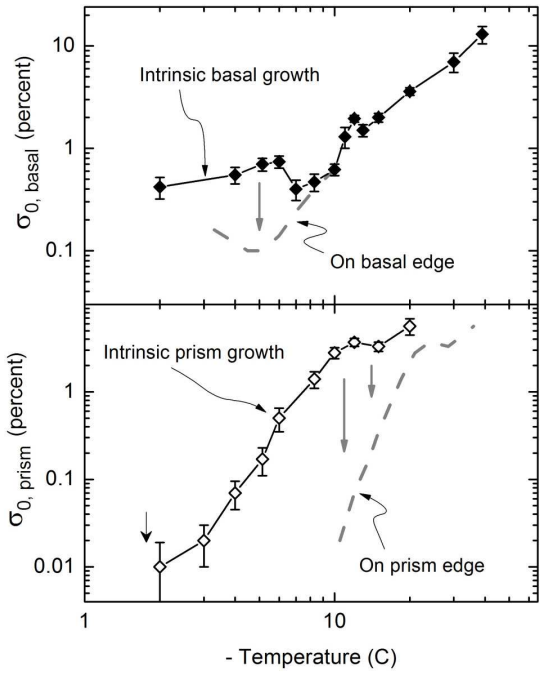

Figure 5: In this graph the solid lines show the intrinsic $\sigma_{0,basal}(T)$ and $\sigma_{0,prism}(T)$ on large facet surfaces, using the data shown in Figure 2. The dotted lines show our proposed $\sigma_{0,basal,SDAK}(T)$ and $\sigma_{0,prism,SDAK}(T)$ when the terrace width is very small, as a result of the SDAK effect, as described in the text.

melting and its accompanying drop in $\sigma_{0,prism}$. The end result is that the tendency to produce thin plate-like crystals is reduced below -20 C, as is observed.

On the other hand, we would expect that the SDAK effect at -10 C on the prism facet would be substantial, since the intrinsic $\sigma_{0,prism}(T)$ continues to drop at still higher temperatures. However, once $\sigma_{0,prism}$ is reduced to values of order 0.1 percent, the nucleation barrier becomes so low that any additional reduction would have little effect on the growth rates. At the same time, $\sigma_{0,basal}$ drops with increasing temperature near -10 C as well. When both $\sigma_{0,basal}$ and $\sigma_{0,prism}$ are low, then the anisotropy in $\alpha_{prism}/\alpha_{basal}$ will decrease, so thin plates no longer form. Putting the pieces together, this qualitatively explains why the formation of thin plates peaks at temperatures around -15 C, as seen in the morphology diagram.

Note that this overall physical picture suggests that there might exist a weaker SDAK effect on the basal facet at -15 C, since $\sigma_{0,basal}$ also drops with increasing temperature. However, as mentioned above, because the SDAK instability favors the growth of thin plates at this temperature, the SDAK effect on the basal facet has little influence on the overall crystal growth morphology. Because this weaker SDAK effect on the basal surface at -15 C is quite uncertain, and moreover it is overshadowed by the SDAK effect on the prism surface at this temperature, is was not included in Figure 5. Nevertheless it may exist, and it may be measurable by other means, so we suggest it

as a possibility for future investigation.

At temperatures near -5 C, our model includes an SDAK instability favoring rapid basal growth and the formation of needles and hollow columns. However, the underlying physical mechanism is quite different from the SDAK effect on the prism surface near -15 C. In our discussion of $\sigma_{0,basal}(T)$ above, we suggested that the formation of a relatively sharp ice/QLL interface on the basal facet caused a positive $d\sigma_{0,basal}/dT$ at -6.5 C, and likewise caused β_{basal} to be considerably higher than β_{prism} at higher temperatures. We further propose that the sharp ice/QLL interface is relatively fragile when the QLL is thin, and therefore the sharp interface becomes unstable when the width of the basal facet is reduced to near molecular dimensions.

In the absence of a sharp ice/QLL interface, we would then expect that $\sigma_{0,basal}$ would diminish with increasing temperature, so that $\sigma_{0,basal}$ is no longer much larger than $\sigma_{0,prism}$. In other words, we would expect that $\sigma_{0,basal}(T)$ on a narrow basal terrace would extrapolate from the behavior at -7 C and lower temperatures as shown in the top panel Figure 5. The details of this extrapolation are uncertain, but are not terribly important for the present discussion; all that matters is that the reduction in $\sigma_{0,basal}$ on a narrow basal terrace near -5 C is sufficient to bring about the SDAK instability that promotes columnar growth.

3.3 Further Investigations of Structure Dependent Attachment Kinetics

Our understanding of SDAK effects and the SDAK instability are rather poor at present, so much work is needed to develop a clearer picture of this phenomenon. The measurements in [37] present a rather strong case that the SDAK instability does exist, at least near -15 C, but little has been done at other temperatures. Our model clearly predicts that the SDAK instability should be present at temperatures near -5 C, and demonstrating this experimentally seems quite straightforward. Investigations of growth behaviors at other temperatures should also be fruitful, and in principle one could map out the SDAK effects over a range of conditions.

Observations of growth behaviors as a function of supersaturation, temperature, air pressure, and initial conditions could all provide useful insights. As was demonstrated in [37], however, quantitative comparisons between growth data and numerical models are essential for making progress in this area. Careful numerical modeling of diffusion-limited growth, accurate growth measurements, and well-defined experimental conditions, are all necessary to disentangle the various processes affecting snow crystal growth rates and morphologies.

4 Discussion

The goal of the present paper is not to have the final word on this subject, but rather to take a significant step forward in defining a comprehensive physical model of snow crystal growth dynamics. Toward this end we believe we have identified many key features in such a model, and we have proposed plausible physical origins for various aspects of the model behavior. Our model is admittedly complex, and we have used some *ad hoc* assumptions to fill in aspects that are not otherwise well constrained. On the plus side, however, our model makes many quantitative predictions that can be tested with targeted experimental investigations. Moreover, our model also suggests theoretical investigations, particularly using molecular dynamics simulations, that may yield important insights. The usefulness of any model is its predictive power, and time will tell how well the model stands up to additional scrutiny.

The first important feature in our model is simply that the transport of water molecules via diffusion through the surrounding background gas plays a substantial role in guiding the growth and morphological evolution of a snow crystal. This conclusion is certainly not new, but the recent development of physically realistic cellular automata methods appears to be a significant breakthrough in modeling the diffusion-limited growth of crystals that are both faceted and branched, as are snow crystals.

A careful look at the diffusion equation shows that the growth of snow crystals under ordinary atmospheric conditions is almost always strongly affected by diffusion effects. Only for micron-scale crystals growing at quite low pressures, or for very slowly growing crystals, is this statement not correct. Moreover, about the only way to model the diffusion-limited growth of snow crystals with adequate accuracy is by employing numerical methods. Without careful diffusion modeling, it is extremely difficult, if not impossible, to experimentally measure snow crystal growth parameters in a reliable fashion. This basic fact has not been adequately appreciated in many previous snow crystal growth experiments.

A second key feature in our model is the central role of the surface attachment kinetics, especially the intrinsic attachment coefficients of the principal facets, α_{basal} and α_{prism}. A successful model must first describe how these parameters depend on temperature T and supersaturation $\sigma_{surface}$, and must provide a reasonable picture of the underlying physical processes responsible for the observed behaviors in $\alpha_{basal}(T, \sigma_{surface})$ and $\alpha_{prism}(T, \sigma_{surface})$. This task, by no means simple, is the first step toward defining a comprehensive model of snow crystal growth dynamics.

In our model we rely on the empirical growth data to define the intrinsic attachment coefficients. These data are well described by a dislocation-free layer-nucleation crystal growth model, which we parameterize as $\alpha(\sigma_{surf}) = A \exp(-\sigma_0/\sigma_{surf})$, and the measured parameters $A(T)$ and $\sigma_0(T)$ for the basal and prism facets are shown in Figure 2. We believe these data are substantially more reliable than previous attempts, in part because careful attention was given to understanding systematic experimental effects arising from particle diffusion, substrate interactions, and other sources.

We attempted to paint a reasonable physical picture explaining the intrinsic growth behavior in our discussion above. While we believe this picture is satisfactory, there may well be other interpretations of the data. This is clearly an area for additional experimentation and theoretical investigations. The ice surface has a complex structure and it is far from being in a static state. Understanding in detail how the structure and dynamics of the ice surface affect crystal growth rates remains a significant challenge.

A third key feature in our model is the importance of structure-dependent attachment kinetics, and this is perhaps the most novel and controversial aspect of what we have presented above. The evidence supporting the SDAK phenomenon has become quite strong, and we believe it is now difficult to deny that SDAK effects are present in snow crystal growth, and that they play a central role in the formation of thin plate-like crystals near -15 C. The details in what we presented above may be inaccurate at some level, and the physical origins we put forth for the SDAK effect may require revision, but we believe that the SDAK effect must be an essential part of any comprehensive snow crystal growth model. Further experimental and theoretical investigations into the SDAK effect and the SDAK instability are likely to provide important new insights into this phenomenon.

Experimental and theoretical efforts focusing on structure formation in ice over the past several decades have continually pushed the remaining frontiers ever closer to the molecular scale. The SDAK instability, the parameterization of the attachment coefficients for the principal facets, as well as the properties of surface melting, all arise from the detailed molecular dynamics at the crystal surface. Since much progress has been made recently in molecular dynamics simulations of

the ice surface, it appears promising that additional investigations along these lines may reveal new insights into ice growth behavior, and especially why the ice surface properties vary with temperature as they do. How these advances apply to other crystal systems, and to our understanding of surface molecular dynamics in general, remains to be seen.

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